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COULOMB'S LAW AND THE QUANTITATIVE

INTERPRETATION OF REACTION RATES, III

by

Edward S. Amis

UNIVERSITY OF ARKANSAS

Department of Chemistry

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ABSTRACT

In the derivation of equations for the effect of
the dielectric constant of the medium upon reaction
rates the use of Coulombic energy rather than Coulombic
free energy as obtained from the electrostatic force
equation is justified thermodynamically in constant
dielectric constant media.

The nature of the electrostatic effect with
respect to whether the effect was favorable or unfavorable
to the rate process is discussed for certain selected
conditions and reactant types.

The integration of the force equation

$$F = - \int_c^r f \, dr$$

gives free energy, F. Amis (1,2,3) has considered the

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1. Amis, Edward S., J. Am. Chem. Soc., 63, 1606 (1941)

2. Amis, Edward S., J. Chem. Educ., 29, 337 (1952)

3. Amis, Edward S., ibid., 30, 351 (1953)

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equation to give energy when the force, f, was used as
Coulomb's force involving ions and ions, ions and

dipoles or dipoles and dipoles when reacting in media of constant dielectric constant.

This paper proposes to show that in media of constant dielectric constant, the change of Coulombic free energy with dielectric constant is equivalent to change of Coulombic energy with change in dielectric constant. Thus the derivations of the rate equations was correctly interpreted as being based on Coulombic energies.

Coulombic free energy F_c, for bringing an ion of charge $Z_1 \epsilon$ from ∞ to a distance r of an ion of charge $Z_2 \epsilon$, is found by inserting in the integral

$$F_c = -\int^r f \, dr \tag{1}$$

the Coulombic expression for the force f between the ions, namely,

$$f = \frac{Z_1 \epsilon Z_2 \epsilon}{Dr^2} \tag{2}$$

and integrating the resulting equation thus

$$F = - \frac{Z_1 \epsilon Z_2 \epsilon}{D} \int_\infty^r \frac{dr}{r^2} = \frac{Z_1 \epsilon Z_2 \epsilon}{Dr} \tag{3}$$

The difference in Coulombic free energy for performing the above operation on a mole of ions in a medium of dielectric constant D_2 as compared to operating in a medium of dielectric constant D_1 is given by the equation

$$\Delta F_c = \frac{N \, Z_1 Z_2 \epsilon^2}{r} \left(\frac{1}{D_2} - \frac{1}{D_1} \right) \tag{4}$$

where N is Avagadro's number.

The free energy change ΔF_D for a process involving the ions in a medium of dielectric constant D_2 is equal to the free energy change ΔF_{D_1} for the process in

medium of dielectric constant D_1 plus the change in Coulombic free energy ΔF_c in transferring the process from medium 1 to medium 2, thus

$$\Delta F_{D_1} = \Delta F_{D_2} + \Delta F_c \tag{5}$$

and a like expression holds for the other thermodynamic functions, for instance

$$\Delta S_{D_2} = \Delta S_{D_1} + \Delta S_c \tag{6}$$

and

$$\Delta E_{D_2} = \Delta E_{D_1} + \Delta E_c \tag{7}$$

Now

$$\Delta F = \Delta H - T\Delta S \tag{8}$$

and for a process in solution where the change of volume is negligable

$$\Delta H = \Delta E + p\Delta V = \Delta E \tag{9}$$

Therefore in solution

$$\Delta F = \Delta E - T\Delta S \tag{10}$$

We have from Eq. (5) and (10)

$$\Delta E_{D_2} - T\Delta S_{D_2} = \Delta E_{D_1} - T\Delta S_{D_1} + \Delta E_c - T\Delta S_c \tag{11}$$

But for chemical rate processes carried out in solvents of constant dielectric constant we have (4) for the change

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4. LaMer, Victor K., J. Franklin Inst., **225**, 709 (1938).

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of entropy ΔS_c due to Coulombic effects

$$\Delta S_c = \frac{\Delta F_c}{T} \left[\frac{\ln D}{\ln T} \right] = 0 \tag{12}$$

and therefore from Eq. (6)

$$T\Delta S_{D_2} = T\Delta S_{D_1} \tag{13}$$

Thus from Eq. (11), (12), and (13)

$$\Delta E_{D_2} = \Delta E_{D_1} + \Delta E_c. \tag{14}$$

also from Eq. (10) and (12)

$$\Delta F_c = \Delta E_c - T\Delta S_c = \Delta E_c. \tag{15}$$

and using Eq. (14) and (15)

$$\Delta E_c = \frac{NZ_1 Z_2 \epsilon^2}{r}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \tag{16}$$

In the case of ionic reactants in solution then

$$k'_{D_2} = Z\, e - \frac{\Delta E_{D_2}}{RT} \tag{17}$$

and

$$\log k'_{D_2} = \log Z - \frac{\Delta E_{D_2}}{2.303\ RT}$$

$$= \log Z - \frac{\Delta E_{D_1}}{2.303\ RT} - \frac{\Delta E_c}{2.303\ RT} \tag{18}$$

But

$$\log k'_{D_1} = \log Z - \frac{\Delta E_{D_1}}{2.303\ RT} \tag{19}$$

therefore

$$\log k'_{D_2} = \log k'_{D_1} - \frac{\Delta E_c}{2.303\ RT} \tag{20}$$

Substituting the expression for ΔE_c from Eq. (16) into Eq. (20), we have

$$\log k'_{D_2} = \log k'_{D_1} - \frac{N\, Z_1 Z_2 \epsilon^2}{2.303\ RTr}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \tag{21}$$

and if dielectric constant D_2 is taken as a reference dielectric constant with a value of infinity and if D_1 is taken as any dielectric constant D, we have from Eq. (21) and remembering that $N/R = 1/k$

$$\log k'_{D=D} = \log k'_{D=\infty} + \frac{Z_1 Z_2 \epsilon^2}{2.303\ kTrD} \tag{22}$$

as was given by Amis (5).

5. Amis, Edward S., J. Chem. Educ., 29, 337 (1953)

Similar considerations apply to the derivations of the
equations for the dielectric constant effect upon the specific
velocity constant of reactions between ions and dipoles and
between dipoles and dipoles (6).

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6. Amis, Edward S., J. Chem. Educ., <u>30</u>, 351 (1953)

In the equations for the different charge type combi-
nations of reactants it proves permissible to account for the
effect upon reaction rates of electrostatic forces by taking
into account the charge signs of the ions and to regard the
moments of dipoles as having only magnitude and no sign. This
seems hard to visualize since although the overall charge on a
dipole is zero and its sign neither positive nor negative, yet
there are positive and negative centers of charge in a dipole
and it seems reasonable that an ion would approach a dipole from
an electrostatically favorable direction, that is, a positive
ion would preferentially approach the negative end of a dipole
and a negative ion would preferentially be attracted to
positive end of a dipole.

The equation derived by Amis (6) for the effect of the
dielectric constant of the medium upon reactions between ions
and molecules is

$$\ln k'_{D = D} = \ln k'_{D = \infty} + \frac{Z \epsilon \mu}{D k T r^2} . \qquad (23)$$

The predictions of this equation, considering only the
magnitude of the dipole moment, μ, of the molecular reactant,
has been found to agree with data in the case of the reactions
of the positive hydrogen-ion with sucrose (6), the negative

hydroxide ion with diacetone alcohol (6), the negative
hydroxide ion with methyl propionate (7), the positive
hydrogen ion with methyl propionate (8), the positive

7. Quinlan, John E., and Amis, Edward S., Data not yet presented for publication.

8. Hockersmith, James Lee, and Amis, Edward S., Anal. Chim. Acta, 9, 101 (1953).

hydrogen ion with ethyl acetate (9) and the negative

9. Nair, P. Madhavan and Amis, Edward S., Anal. Chim. Acta 9, 111 (1953)

thiosulfate ion reacting with ethyl bromomalonate (10).

10. Broach, Wilson J., and Amis, Edward S., accepted for publication in J. Chem. Phys.

The rates of the reactions involving the positive ionic
reactants decrease with increasing dielectric constant
while the rates of the reactions in which negative ionic
reactants occur increase with increasing dielectric
constant of the media. Furthermore the plots of $\log k'_{D=D}$
versus $1/D$ are straight lines, the magnitudes of the
slopes of which, when their signs and the charge sign of
the ions are accounted for, yield reasonable molecular
dimensions for the parameter r, which is supposedly the
distance of approach of reactants for reaction to occur.

Electrostatically the above phenomena might be
explained as follows. A positive ion tends to approach

the negative end of a molecule. There is an attractive
force operative which is diminished by an increase of the
dielectric constant. Thus the rate of the reaction
decreases as the dielectric constant increases. Apparently
the cation reactant tends to approach the dipolar reactant
from an electrostatically favorable direction. In the
case of the negative ionic reactant, if the ease of approach
of the ion to the molecule is the factor which governs
the electrostatic influence on the reaction rate, the
approach of the ion to the dipolar molecule would have
to be electrostatically unfavorable for the rate to
increase with increase of the dielectric constant. Because
whether favorable or unfavorable the electrostatic force
which determines the ease of approach of two electric
charges, would decrease with increase of dielectric
constant, and a decreased influence of an unfavorable
approach only could account for an increase of rate.

Let us now consider the reaction of a dipolar mole-
cule with a dipolar molecule. Laidler and Eyring (11)

11. Laidler, K. J., and Eyring, Henry, "The Theory of
Rate Processes," McGraw-Hill Book Company, New York,
1941, p. 442.

summarize the dielectric constant effect upon such
reactions by indicating an increase of reaction rate
with increasing dielectric constant. Their equation which
gives the influence of dielectric constant upon the
reaction rate for dipolar molecule-dipolar molecule
reactions is (12)

must be an unfavorable one and the dipolar molecule
reactants must approach each other from an electrostatically
unfavorable direction if approach is the controlling
electrostatic effect.

Also in the Amis equation (6) for dipolar molecule-
dipolar molecule reactions, namely,

$$\ln k'_{D=D} = \ln k'_D = -\frac{2 \mu_1 \mu_2}{Dk Tr^3} \qquad (25)$$

the electrostatic term is preceded by a negative sign and
must decrease in absolute values as D increases for
$\ln k'_{D=D}$ to increase with increasing D. Thus again the
electrostatic effect is unfavorable and the dipolar
reactants must approach each other from an electro-
statically unfavorable direction if approach is the
governing electrostatic effedt.